A calculable and quasi-practical gas

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Abstract

A new kinetic approach is developed and a quasi-practical gas is defined to which the new approach can be applied. One of the advantages of this new approach over the standard one is direct calculability in terms of today's computational means.

PACS 51.10.+y - Kinetic and transport theory of gases

1 Introduction

The impressive progress of nonlinear science in the last several decades revealed a large number of structures and mechanisms that were novel and fascinating to almost all of us. This has, in a sense, suggested that several aspects of our existing statistical theory, whose first kinetic equation was proposed more than a century ago, need certain kinds of 'upgrade' or 'renewal'.

In some of our relatively recent papers[1, 2], we were tempted to analyze the standard kinetic theory from different perspectives. It was argued that (i) in various artificial and realistic situations, distribution functions of gases may have very unconventional structures: they can be, for instance, discontinuous at every and each spatial point and thus the usual differential apparatus becomes inapplicable (after all, there are indeed many structures and mechanisms in nature to which the use of the usual differential apparatus is quite limited); and that (ii) while the left side of the Boltzmann equation is symmetric in terms of partial derivatives with respect to the position and velocity, the right side of the equation is constructed entirely in the velocity space (the position coordinates merely serve as inactive parameters), which is incomprehensible especially in the mathematical sense.

The major objective of this work is, however, rather practical: to define a kinetic gas and, at the same time, to find out an algorithm which can be used to calculate the behavior of the gas rather completely. It is hoped that if such study gets established somehow, further studies, either concerning the foundation of the existing statistical theory or concerning the development of more general treatment, will be inspired and promoted.

The structure of this paper is the following. In Sect. 2, we propose our working model, a gas leaking out of a container, resembling the cavity model for the black-body radiation. In Sect. 3, the zeroth-order distribution function of the leaking gas is formulated and, in passing, it is shown that distribution

functions of real gases may have radically discontinuous structures untreatable for the standard theory. In Sect. 4, the collisional correction is investigated with help of a methodology that is slightly different in form but much different in concept from the standard treatment. In Sect. 5, we further comment on why the distribution function averaged over finite velocity solid-angle ranges needs to be introduced. Sect. 6 summarizes the paper.

2 A leaking gas

At the kinetic level, one of the customary conceptions about calculating a practical gas is to solve the Boltzmann differential-integral equation with help of a difference scheme. Known difficulties associated with this conception may be summarized as follows.

1. There are seven variables: time, three spatial coordinates and three velocity components. If we divide each variable into N intervals, 'the degrees of freedom' of the system are N^7. To reveal the true properties of a nonequilibrium phenomenon, such as those related to a turbulence, N has to be rather large and N^7 has to be terribly huge, so that no today's computational means really helps.

2. The complex nature of the collisional operator in Boltzmann's equation makes the situation worse.

3. Boundary conditions and initial conditions impose extra problems. As to a differential equation, well specified boundary and initial conditions usually mean that a uniquely and clearly defined solution can be constructed, say, from a difference scheme. (The uniqueness may not be truly desired in view of the fact that bifurcations take place in nature.) As to an integral equation, boundary and initial conditions may be specified rather loosely and it leaves us certain room to 'manipulate'. Boltzmann's equation is a differential-integral equation and it is not entirely clear in which direction we should go.

Due to these difficulties (and possibly many more), almost no realistic problems have been fully treated, let alone conclusive comparison between the kinetic theory and realistic experiments.

Interestingly enough, the aforementioned difficulties, at least some of them, are not intrinsic to the dynamics that we wish to study. In some sense, if the standard approach had not dominated our mind too strongly, we might have already had workable alternative approaches, at least for some special cases. In what follows, we shall try to substantiate this viewpoint.

We consider a gas consisting of hard spheres and confined to a closed container. The interactions between the walls and particles, and between the particles themselves, make the gas solidly and quickly in equilibrium. Namely, the

probability of finding particles in a phase volume element $d\mathbf{r}d\mathbf{v} = dxdydzdv_xdv_ydv_z$ takes its Maxwell form

$$f_M \equiv n_0 \left(\frac{m}{2\pi\kappa T}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2\kappa T}\right), \tag{1}$$

where m is the mass of particle, κ the Boltzmann constant, T the temperature of the gas and n_0 the particle density in the container.

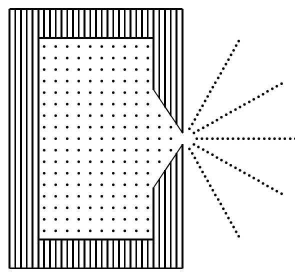

Figure 1: Schematic of a leaking gas.

We then suppose that there is a small hole on the wall of the container, as shown in Fig. 1. The aim of our formalism is to determine the distribution function of the leaking gas. For convenience of discussion, it is further assumed that (i) the hole is indeed small so that the leaking is relatively slow and the relevant distribution function can be considered to be time-independent; (ii) since the regions far from the hole are kept in the vacuum state (by a pump for instance), no incoming particles need to be taken into account; and (iii) the leaking gas outside the container is so dilute that the zeroth-order solution can be determined by the collisionless trajectories of particles while the first-order correction can be formulated by assuming the particles of the leaking gas to collide with each other once and only once.

3 The zeroth-order distribution function

If we ignore the particle-to-particle interaction and ignore the gravitational force acting on each particle, the collisionless motion of every particle of the leaking gas is conceptually simple—moving along a straight line. However, it is still necessary and interesting to express the corresponding distribution function in a proper mathematical form.

We start our discussion with the conventional theory. The theory states that the distribution function satisfies, with collisions ignored completely,

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \mathbf{v}} = 0, \tag{2}$$

where $\mathbf{F}$ represents the external force. Equation (2) is sometimes termed the collisionless Boltzmann equation[3]. A natural notion related to such terminology is that any procedure, a difference scheme for instance, if applicable in solving the regular Boltzmann equation, must be applicable in solving this reduced equation. Strangely, complicated and subtle issues arise from this 'natural' notion; and we shall discuss these issues at the end of this section.

To formulate the zeroth-order distribution function, the following 'slightly different' approach is helpful. Rewriting Equation (2) along a particle path in the phase space, we arrive at the path invariance[3, 4]

$$\left.\frac{df}{dt}\right|_{\text{path}} = 0. \tag{3}$$

As far as our leaking gas is concerned, this means $f|_{\text{path}} = f_M$, where f_M has been defined by expression (1).

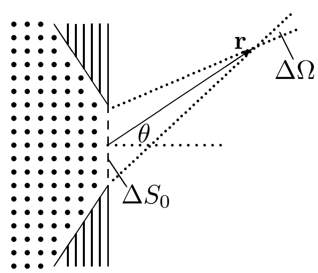

Figure 2: The velocity distribution at the position $\mathbf{r}$.

Then, it seems that the zeroth-order distribution function on the right side of the hole is uniformly identical since any spatial point there is reachable along a path radiating from the inside of the container (the external force is zero and the paths in the phase space and in the spatial space are the same). This notion is, however, rather misleading. By moving together with a particle of the leaking gas, an observer easily realizes that the true particle density around him becomes lower and lower. With this realization in mind, it can easily be found that the distribution function of the leaking gas is strongly limited in the velocity space: the farther from the hole the stronger the limitation is. Namely, as shown in Fig. 2, the true implication of (3) is

$$f(\mathbf{r},\mathbf{v}) = \left\{ \begin{array}{ll} f_M & \text{the direction of } \mathbf{v} \text{ within } \Delta\Omega \\ 0 & \text{otherwise} \end{array} \right. , \tag{4}$$

where $\Delta\Omega$ is a solid-angle range whose size is defined by the solid-angle range

$$\frac{\Delta S_0 \cos\theta}{r^2} \quad \text{with} \quad r = |\mathbf{r}| \tag{5}$$

and whose direction is defined by the position vector $\mathbf{r}$ (with the origin at the hole). Heuristically and intuitively, it can be said that the velocity distribution at every point there is a sting-like function. In almost all the regions on the right side of the hole, where r is relatively large or $\cos\theta$ is relatively small, the stings tend to be infinitely acute.

Though (4) and (5) correctly describe the distribution function, there are some kinds of inconvenience in applying them in analytical calculations. For practical and theoretical reasons, we wish to express the distribution function $f(\mathbf{r},\mathbf{v})$ directly and explicitly in terms of $\mathbf{r}$ and $\mathbf{v}$.

To get such expression, we adopt the picture that the sting-like velocity distributions of the leaking gas are indeed infinitely acute, either by assuming the hole to be truly small or by assuming the interested region to be truly distant. Under this understanding, we can use a δ-function to reflect the limitation of the distribution function in the velocity space and replace (4) and (5) by

$$f(\mathbf{r},\mathbf{v}) \equiv g(r,v)\delta\left(\Omega_{\mathbf{v}} - \Omega_{\mathbf{r}}\right) \tag{6}$$

with

$$g(r,v) = n_0 \left(\frac{m}{2\pi\kappa T}\right)^{3/2} e^{-\frac{mv^2}{2\kappa T}} \frac{\Delta S_0 \cos\theta}{r^2},$$

where $\Omega_{\mathbf{v}}$ is the solid angle in the direction of $\mathbf{v}$ and $\Omega_{\mathbf{r}}$ is the solid angle in the direction of $\mathbf{r}$. Expression (6) enables us to do analytical calculation easily. For instance, with help of it we may compute the zeroth-order particle density outside the container by

$$n(\mathbf{r}) = \int f(\mathbf{r},\mathbf{v})d\mathbf{v} = \int f v^2 dv d\Omega = n_0 \frac{\Delta S_0 \cos\theta}{4\pi r^2}, \tag{7}$$

which is quantitatively consistent with our intuitive notion about the particle density outside the container.

Before leaving this subject, we go back to discuss several usual concepts concerning the collisionless and regular Boltzmann equations. It is commonly believed that the collisionless Boltzmann equation (2) is completely equivalent to the path-invariance expressed by (3). In our view, this equivalence is just a formal one. For one thing, expression (3) makes sense strictly along a particle path, which is governed by the collisionless motion equations of single particle; while Boltzmann's equations are supposed to be solved by a difference scheme with help of boundary and initial conditions in which trajectories of individual particle do not play any role. For another, unconventional topology and dynamics are related to (3). Distribution functions described by it, such as (4) and (6), can be shaped like stings; more than that, these stings 'spread' out along paths of particles, become sharper and sharper when spreading, and continue to spread out after being infinitely sharp. (Distributions produced by boundaries can be even 'sharper', see Sect. 5.) Boltzmann's equations, being ones containing differential terms, are not compatible with these 'radical' things.

4 The collisional correction

In this section, we try to deal with collisions. To make our discussion involve less details, we shall only formulate the first-order correction. Namely, it is assumed that the particles expressed by (6) will collide once and only once (although further extension can be made with no principal difficulty).

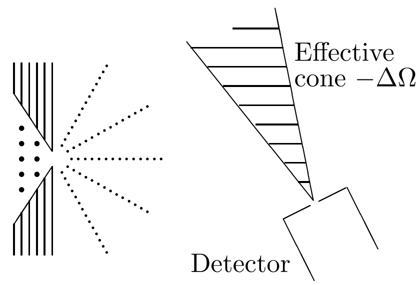

Figure 3: A particle detector is placed in the leaking gas.

What can be measured in an experiment should be of our first concern. For this reason, we consider a particle detector placed somewhere in the leaking gas and try to determine how many particles will be recorded by the detector, as illustrated in Fig. 3. There are several essential things worth mentioning about the detector.

1. The opening allowing particles to enter the detector is considered to be sufficiently small. Or, in the mathematical language, we regard the area of the opening, denoted by ΔS, as an infinitesimal quantity throughout this section.

2. Without specifying concrete structure and mechanism of the detector, it is assumed that every particle that enters the detector and is in the velocity range
$$\Delta \mathbf{v} = \Delta v v^2 \Delta\Omega, \tag{8}$$
where Δv and $\Delta\Omega$ are predetermined before the measurement, will be recorded, and every other particle will not.

3. While ΔS and Δv are allowed to shrink to zero, we define $\Delta\Omega$ as a finite solid-angle range. As will be seen, the discrimination against $\Delta\Omega$ is taken almost entirely by necessity.

If the detector works as described above, do we know the distribution function at the entry of the detector? The answer to it is almost a positive one. If ΔN is the number that the detector counts during Δt, the particle density in

the phase volume element $(\Delta S v \Delta t)(\Delta v v^2 \Delta\Omega)$ is

$$f(t, \mathbf{r}, \mathbf{v}, \Delta\Omega) \approx \frac{\Delta N}{(\Delta S v \Delta t)(\Delta v v^2 \Delta\Omega)}. \tag{9}$$

The form of (9) illustrates one of the most distinctive features of this approach: it tries to calculate the distribution function directly rather than to formulate a dynamic equation concerning how many particles enter and leave a phase volume element. Apart from other advantages, this brings to us a lot of convenience in computational terms.

Noticing that only the collisions taking place within the shaded spatial cone $-\Delta\Omega$, which is equal and opposite to the velocity cone $\Delta\Omega$, can possibly contribute to ΔN, as shown in Fig. 3, we call the region inside $-\Delta\Omega$ the effective cone. Since this effective cone is a finite one ($\Delta\Omega$ is finite), our primary task is to divide it into many subregions, denoted by $d\mathbf{r}'$ (the origin of the coordinates is still at the center of the hole as in Sect. 3), and to calculate how collisions in each of the subregions give contribution to ΔN.

Consider that two beams of identical particles (but still distinguishable in terms of classical mechanics)

$$f(t', \mathbf{v}', \mathbf{r}')d\mathbf{v}' \quad \text{and} \quad f(t', \mathbf{v}_1', \mathbf{r}')d\mathbf{v}_1' \tag{10}$$

collide within $d\mathbf{r}'$ and at time t', producing particles with velocities $\mathbf{v}$ and $\mathbf{v}_1$ respectively. It is noted that there is a time delay

$$t - t' = \frac{|\mathbf{r} - \mathbf{r}'|}{v} \quad \text{with} \quad v = |\mathbf{v}| \tag{11}$$

between the time of collision and the time of detection. Since the leaking is assumed to be relatively slow (or the gas inside the container is supplied by an external gas source), we think of our problem as a time-independent one and pay no more attention to the time variable hereafter. To better observe the collisions, we define

$$\begin{cases} \mathbf{v}' + \mathbf{v}_1' = 2\mathbf{c}' \\ \mathbf{v}' - \mathbf{v}_1' = 2\mathbf{u}' \end{cases} \quad \text{and} \quad \begin{cases} \mathbf{v} + \mathbf{v}_1 = 2\mathbf{c} \\ \mathbf{v} - \mathbf{v}_1 = 2\mathbf{u} \end{cases}. \tag{12}$$

That is to say, by virtue of the conservation laws of energy and momentum, $\mathbf{c} = \mathbf{c}'$ represents the velocity of the center-of-mass and $u = |\mathbf{u}| = |\mathbf{u}'|$ stands for the particle speed relative to the center-of-mass. Examining the beam-to-beam collision in the center-of-mass frame, we find that the differential number of the colliding particles is

$$[d\mathbf{r}' f(\mathbf{r}', \mathbf{v}')d\mathbf{v}'][f(\mathbf{r}', \mathbf{v}_1')d\mathbf{v}_1'][2u\sigma_c(\mathbf{u}', \mathbf{u})d\Omega_c \Delta t], \tag{13}$$

where Ω_c is the solid angle between $\mathbf{u}'$ and $\mathbf{u}$ and σ_c is the cross section associated with particles emerging within the solid-angle range $d\Omega_c$. By integrating (13)

and getting help from (6), the right side of (9) is equal to

$$\int_{-\Delta\Omega} d\mathbf{r}' \int_{\Delta v\Delta\Omega_0} d\Omega_c \int_0^\infty dv' \int_0^\infty dv_1' \frac{2u\sigma_c g(r',v')g(r',v_1')}{(|\mathbf{r}-\mathbf{r}'|^2\Delta\Omega_0 v)(v^2\Delta v\Delta\Omega)}, \tag{14}$$

where $\Delta\Omega_0$ is the solid-angle range formed by the point $d\mathbf{r}'$ (as the apex) and the detector opening ΔS (as the base), and the subindex $\Delta v\Delta\Omega_0$ there states that only particles that can be recorded by the detector will be taken into account. Since the size of $\Delta\Omega_0$ is 'much smaller' than that of $\Delta\Omega$, every particle starting its journey from the effective cone and entering the detector will be treated as one within $\Delta\Omega$. With help of the variable transformation from (v', v_1') to (c', u') and finally to (c, u), we rewrite expression (14) as

$$\int_{-\Delta\Omega} d\mathbf{r}' \int_{\Delta v\Delta\Omega_0} d\Omega_c \int_0^\infty dc \int_{-c}^{c} du \frac{2u\sigma_c \cdot \|J\| \cdot g(c+u)g(c-u)}{(|\mathbf{r}-\mathbf{r}'|^2\Delta\Omega_0 v)(v^2\Delta v\Delta\Omega)}, \tag{15}$$

in which the Jacobian between the variable transformation is

$$\|J\| = \frac{\partial(v', v_1')}{\partial(c, u)} = 2. \tag{16}$$

In view of the symmetry of the cross section there, we have

$$\int_{-c}^{c} du \cdots = 2\int_0^c du \cdots. \tag{17}$$

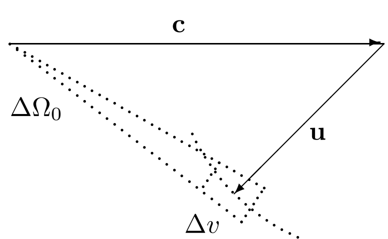

Figure 4: The relation between the velocity element $v^2\Delta v\Delta\Omega_0$ and the velocity element $u^2 du d\Omega_c$.

And, by investigating the situation in the velocity space shown in Fig. 4, the following relation can be found out:

$$\int_{\Delta v\Delta\Omega_0} u^2 du d\Omega_c \cdots \approx v^2 \Delta v \Delta\Omega_0 \cdots. \tag{18}$$

Therefore, the first-order distribution function at the entry of the detector is

$$f(\mathbf{r}, \mathbf{v}, \Delta\Omega) = \frac{1}{v\Delta\Omega} \int_{-\Delta\Omega} d\mathbf{r}' \int_0^\infty dc \frac{8\sigma_c(\mathbf{u}', \mathbf{u}) g(r', c+u) g(r', c-u)}{u|\mathbf{r}-\mathbf{r}'|^2}, \tag{19}$$

in which, although $u = |\mathbf{c} - \mathbf{v}|$, $u < c$ needs to be ensured for the integral to make sense and the direction of $\mathbf{u}'$ is the same as that of $\mathbf{c}'$ or $\mathbf{c}$.

Since we have, at the beginning of this section, assumed $\Delta\Omega$ to be a finite solid-angle range, expression (19) is nothing but the distribution function averaged over $\Delta\Omega$, which is, in a sense, still different from 'the true and exact distribution function' there. In the next section, we shall come back to this issue and find out that the true and exact distribution function is actually beyond our reach.

If interested, readers may test the resultant formalism with aid of realistic and computational experiments or develop it to cover more practical and more complicated cases. This is one of the major purposes of the present paper.

5 Discussion

In this section, we wish to further justify one of our introduced concepts, the distribution function averaged over finite solid-angle ranges of velocity.

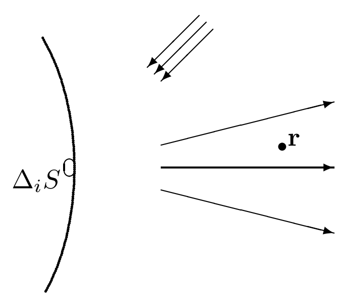

Figure 5: Particles refleted by a surface.

Let's look at the path-invariance theorem expressed by (3) again. Although the path-invariance is not equivalent to the collisionless Boltzmann equation (see the remark at the end of Sect. 3), the theorem can still be thought of as a part of the conventional theory since it is formally the same as the collisionless Boltzmann equation and it is consistent with the usual notion that distribution functions of real gases are continuous or, at least, piecewise continuous. Then, a crucial question arises. Are all distribution functions of realistic gases continuous or, at least, piecewise continuous? If this is the case, we will be able, at least in principle, to determine the exact distribution function. To see what the real situation is, we examine the case illustrated in Fig. 5, where particles are moving toward a surface with a definite velocity (or, equivalently, let the surface move toward the particles). Since the surface is not uniform geometrically and physically, we need to, in order to formulate the reflected particles, divide it into many small surface elements, denoted by $\Delta_i S$ herein. It is easy to see that,

corresponding to one of $\Delta_i S$ the reflected particles are like ones emitted from a point particle source and the distribution function, at a position $\mathbf{r}$ around the surface, is

$$\Delta_i f = \frac{\eta_i(\mathbf{v})\Delta_i S}{4\pi|\mathbf{r}-\mathbf{r}_i|^2}\delta\left(\Omega_{\mathbf{v}} - \Omega_{\mathbf{r}-\mathbf{r}_i}\right), \tag{20}$$

where $\mathbf{r}_i$ represents the position vector of $\Delta_i S$ and $\eta_i(\mathbf{v})$ is the reflection (emission) function that can be determined by experiments[5]. As has been illustrated in Sect. 3, the distribution function expressed by (20) is an infinitely thin 'sting' at every spatial point, and the particle density along a particle path is no longer invariant. The total distribution function at $\mathbf{r}$ is

$$f = \sum_i \Delta_i f = \sum_i \frac{\eta_i(\mathbf{v})\Delta_i S}{4\pi|\mathbf{r}-\mathbf{r}_i|^2}\delta\left(\Omega_{\mathbf{v}} - \Omega_{\mathbf{r}-\mathbf{r}_i}\right). \tag{21}$$

It is then found that, if the true and exact distribution function is indeed of our concern, the δ-functions in (21) will stay there and no regular functions can be used to replace them because each of $\Omega_{\mathbf{r}-\mathbf{r}_i}$ in it points in a distinctive direction, which means, in a more vivid language, the velocity distribution at every spatial point is shaped like an infinite number of infinitely thin stings (similar to functions dealt with in the studies of fractals). Without introducing the distribution function averaged over velocity solid-angle ranges, we will have great difficulty in setting up a calculable theory.

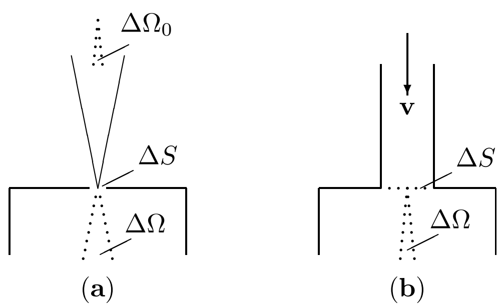

Figure 6: The effective region above the detector: (a) If $\Delta\Omega$ is fixed and ΔS shrinks to zero, it is cone-shaped. (b) If ΔS is fixed and $\Delta\Omega$ shrinks to zero, it is cylinder-shaped.

Treatment of particle-to-particle interactions is always an indispensable chapter of statistical mechanics. While referring readers to elsewhere[1, 2] for analyses of perplexing problems in the textbook methodology, we shall here comment on our own treatment of collision presented in the last section. At first glance, if $\Delta\Omega$ there were infinitely small, both the denominator and numerator of (19) would tend to zero simultaneously and the total expression would remain finite and valid. A careful inspection, however, tells us that there are two 'competing'

quantities $\Delta\Omega$ and ΔS. If we fix $\Delta\Omega$ and let ΔS approach zero, the effective region is a cone-shaped one, shown in Fig. 6a, and the related distribution function is, as has been formulated, the one averaged over the finite solid-angle range $\Delta\Omega$. Whereas, if we fix ΔS and let $\Delta\Omega$ approach zero, the situation is rather different: the effective region becomes a cylinder-shaped one, shown in Fig. 6b, and the related distribution function will be, if formulated, the one averaged over the finite spatial area ΔS. In both the above situations, each of the results is related to an integration, each of the integrations is taken over a region infinitely-extended in space. (Even if more collisions are taken into account the above assertion still holds its significance since particles from the remote regions can still come freely in terms of probabilities.) There is no way to ensure the continuity of each formalism let alone the consistency between the two formalisms.

The discussions in this section clearly show that, in dealing with both collisionless dynamics and collisional dynamics, a finite range of certain variable (whether in the position space or in the velocity space) and the average over this range have to be employed. If the approach is inherently and completely that of differentiation, which means that the exact distribution function is of concern and every position and velocity range must shrink to zero, insurmountable conflicts surface automatically in one way or another. The repetitive appearances of conflict remind us of the situation in quantum mechanics where the accurate position and momentum cannot be determined simultaneously. Possible implication of this issue has yet to be explored.

6 Summary

We have proposed a gas as our working model and formulated a feasible method to calculate it. The formalism shows that real gases, at least certain types of them, can be calculated at the kinetic level. It is expected that such calculations will soon be compared to realistic or computational experiments.

In this paper, collisional effects were investigated under the assumption that each particle involves, at most, one collision. If more collisions are taken into account, the trajectory of a particle will be very much like that of the Brownian motion or, in another sense, similar to that appearing in the logistic map of nonlinear studies. Although the extensions in this direction have been tried[6, 7], it is not appropriate to comment on them before this work is admitted by more in this community.

Helpful discussions with professors Hanying Guo, Ke Wu and Qiang Chen are greatly appreciated. This paper is supported by School of Science, BUAA, PRC.

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